Hindawi
International Journal of Chemical Engineering
Volume 2021, Article ID 9964291, 10 pages
https://doi.org/10.1155/2021/9964291

Research Article

Photocatalytic Degradation of Trifluralin in Aqueous Solutions by UV/$S_2O_8^{2-}$ and UV/ZnO Processes: A Comparison of Removal Efficiency and Cost Estimation

Fatemeh Sadeghi,[1] **Abdolmajid Fadaei**,[2] **Fazel Mohammadi-Moghadam**,[2] **Sara Hemati**,[2] **and Gashtasb Mardani**[3]

[1]*Research Committe, Research Center, Shahrekord University of Medical Sciences, Shahrekord, Iran*
[2]*Department of Environmental Health Engineering, School of Public Health, Shahrekord University of Medical Sciences, Shahrekord, Iran*
[3]*Medical Plants and Cellular and Molecular Research Center, Shahrekord University of Medical Sciences, Shahrekord, Iran*

Correspondence should be addressed to Abdolmajid Fadaei; ali2fadae@yahoo.com

Received 4 March 2021; Revised 31 March 2021; Accepted 4 May 2021; Published 11 May 2021

Academic Editor: Ho SoonMin

Trifluralin is one of the most widely used herbicides, being accounted as the cause of cancer in human. In the present research, the UV/$S_2O_8^{2-}$ and ZnO/UV processes' efficiency in the removal of trifluralin was investigated. A lab scale equipped with a UV lamp was applied. The parameters were studied, including initial trifluralin concentration (0.4–1.2 mg/L), contact time (20–60 min), $S_2O_8^{2-}$ concentration (20–60 μM), and ZnO concentration (50–150 mg/L). The remained trifluralin concentration was measured by HPLC. This study proved the trifluralin removal of 92.90 ± 1.6% and 87.91 ± 19.22% for UV/$S_2O_8^{2-}$ and UV/ZnO processes in the best operation conditions (contact time of 60 min, the persulfate concentration of 40 μM, and the ZnO concentration of 100 mg/L). The optimal trifluraline concentrations were 1.2 mg/L and 0.6 mg/L for UV/$S_2O_8^{2-}$ and UV/ZnO processes, respectively. In both processes, the removal efficiency of trifluralin increased significantly with increasing contact time. The findings exhibited that both processes UV/$S_2O_8^{2-}$ and UV/ZnO followed the zero-order kinetic. The electrical energy consumed of UV/$S_2O_8^{2}$ and UV/ZnO was about 43.95 and 20.41 Kwh/kg, respectively. The results show that UV/$S_2O_8^{2-}$ and ZnO/UV processes were appropriate as the effective treatment method for trifluralin removal. Therefore, it is proposed to study the performance of these processes as an environmentally friendly practice in full scale with real wastewater.

1. Introduction

Pollution of the environment by pesticides has been proven throughout the world. Runoff from urban areas, the return of water to the mainstream, and the washing of agricultural land are the major contributors to this pollution [1, 2]. Weeds have an adverse effect on yield and quality of agricultural product [3]. The most widely method to control weeds and improve the priority growth of the desired crops is application of herbicides. Recently, the application of herbicide has been forbidden in world, but they are widely used in developing countries [4]. Trifuralin (Treflan) is a preemergence herbicide which is used in the farming to control the insects in plantations [4]. The chemical structure of trifuralin is shown in Figure 1. In 2015, more than 4608 tons of trifuralin were used in America, and in 2010, 2540 tons were used in China [2]. The major part of the used trifuralin fails to reach the target site or runoff into the environment, which leads to negative effects on the ecosystem [5]. In recent years, this toxin has become a major environmental concern due to adverse effects on health, including various physiological changes and effects on endocrine genes, kidney damage, fetal weight loss, and increased abortion in animal studies. In addition to the toxicity

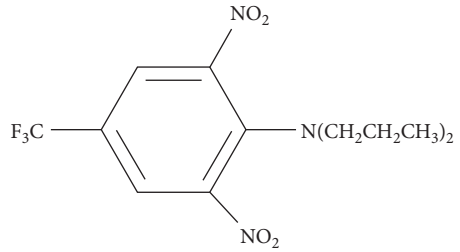

Figure 1: Chemical structures of trifluralin [5].

in mammals, carcinogenicity in humans has been proven due to exposure to this pesticide in the European Union [6, 7]. The United States has classified trifluralin in group C of human carcinogenic substances [1]. According to the WHO and Institute of Standard and Industrial Research of Iran (ISIRI), the Maximum Contaminant Level (MCL) of trifluralin is 0.02 mg/L in drinking water [8], and based on the European Environment Agency, the annual average concentration of this herbicides is 0.03 μg/L [9, 10]. These herbicides are added to soil to prevent their evaporation. Therefore, groundwater contamination may be related to agricultural drainage. Additionally, point sources, including leakage or improper disposal, may cause groundwater contamination. Pendimethalin and trifluralin were often found in groundwater where the preparation, loading, and mixing of herbicides were performed [11]. Among the various technologies for pesticide treatment, advanced oxidation processes have been mainly used for trifluralin degradation which include photolysis in presence of hydroxyl radicals, direct photolysis in presence of UV, and hydrogen peroxide and ozonation [12–15]. Advanced oxidation has high oxidizing properties due to producing free radicals in an aquatic environment, leading to decomposition of pesticides in water [16, 17]. The synthesis process of persulfates ($K_2S_2O_8$) and ultraviolet radiation has been widely considered and is a very efficient technology for eliminating organic pollutants [18]. Persulfate is a very strong oxidant ($E^\circ = 2.1$ V), which is not selectively reactive and is relatively stable at room temperature. Radicals can oxidize toxic and resistant organic compounds, but at room temperature, the decomposition rate is small and, therefore, a catalyst is needed. An activation operation is carried out by UV radiation, ions, electrolysis, and transition metals [6]. Under the activation of UV light, persulfate (PS, $S_2O_8^{2-}$) is most commonly used for the production of $SO_4^{\bullet-}$. In addition, $SO_4^{\bullet-}$ has relatively lower reactivity with natural organic matter and is, thus, considered more suitable for the removal of organic contaminants in an aquatic environment [19]. Through the recent two decades, a considerable amount of attention has been paid to photocatalysis using semiconducting materials such as ZnO due to high optical sensitivity, high stability, nontoxic nature, and higher efficiency in electron production. ZnO with a 3.2 kV band gap and wavelength of 387 nm can be excited under irradiation in the UVA range of 320–380 nm [20, 21]. Previous studies compared the catalytic activity of ZnO and TiO_2 for the degradation of sulfamethazine and chloramphenicol, respectively, and reported that ZnO was slightly more effective than TiO_2 [22, 23]. The performance mechanism of these processes is that the semiconductor material is irradiated with ultraviolet radiation which stimulates the electron from the valence band to the conduction band causing the release of radical hydroxyl [24, 25]. According to the studies conducted so far, no report on trifluralin removal using two methods simultaneously including UV/$S_2O_8^{2-}$ and UV/ZnO processes have been reported. This study aimed to provide two methods for removing pollutants without deteriorating the environmental safety of trifluralin, to determine the association of initial trifluralin concentration, contact time, $S_2O_8^{2-}$ concentration for the UV/$S_2O_8^{2-}$ process, and ZnO dose for UV/ZnO processes. The main objective of this research is the photocatalytic degradation of trifluralin in aqueous solutions by UV/$S_2O_8^{2-}$ and UV/ZnO processes and comparison of removal efficiency and economical nature of these processes.

2. Experimental

2.1. Reagents and Supplies. Trifluralin (α, α, α-trifluoro-2, 6-dinitro-N, N-dipropyl-p-toluidine, $C_{13}H_{16}F_3N_3O_4$) herbicide standard was purchased from Sigma-Aldrich Company. ZnO with a purity of 99% (BET:12 m^2/g), hydrochloric acid and sodium hydroxide, sodium sulfate 99%, N-hexane, acetonitrile, and 99.8% ethanol were purchased from Merck Company, Germany. Figure 2 illustrates the SEM of ZnO nanoparticles. The SEM images of ZnO nanoparticles suggest its particle size as <0.1 μm.

2.2. Experiment. All experiments were carried out in a quartz reactor with a diameter of 5 cm and a 25 cm height with a capacity of 250 ml, equipped with a UV lamp with a wavelength of 254 nm and a power of 6 watts. A magnetic stirrer was used at 150 rpm to mix the reactor contents. In order to prevent the temperature increase, the chemical reactor was placed in a cylindrical container equipped with an inlet and outlet water flow, and the use of an aluminum foil prevented the permeation of ambient light into the reactor. The parameters were studied, including initial trifluralin concentration (0.4, 0.6, 0.8, 1, and 1.2 mg/L), contact time (20, 40, and 60 min), $S_2O_8^{2-}$ concentration for UV/$S_2O_8^{2-}$ processes (20, 40, and 60 μM), and ZnO concentration for UV/ZnO processes (50, 100, and 150 mg/L). The optimal pH was obtained from other studies [26, 27]. The optimal pH of the samples was adjusted at 9 using 0.1 N H_2SO_4 or 0.1 N NaOH. The effect of these parameters on trifluralin removal was investigated by UV/$S_2O_8^{2-}$ and UV/ZnO processes.

2.3. Analytical Methods. At the end of each step, the residual concentration of trifluralin was measured using HPLC (LC-10AT VP) Shimadzu equipped with Phenomenex Gemini 5 lm C18 110A (250–4.6 mm). Trifluralin was identified using the isocratic method with acetonitrile and deionized water (75%: 25% v/v). The injection volume into the system was

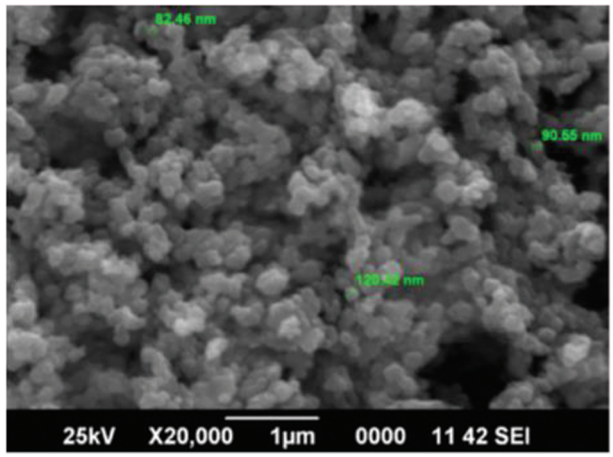

Figure 2: Typical SEM image of ZnO of approx. 10×10^{-2} μm-size particles.

2 ml. Then, the percentage of trifluralin removal was calculated by the following equation:

$$\mathrm{E}(\%) = \frac{(C_0 - C_t)}{C_0}, \quad (1)$$

where C_0 and C_t are the initial and final concentrations of trifluralin, respectively.

3. Results and Discussion

3.1. Effect of Persulfate and ZnO Concentration. In advanced oxidation processes, one of the effective factors in the removal of organic compounds is the concentration of oxidizing matter [28]. In this study, the effect of persulfate and ZnO concentration in UV/$S_2O_8^{2-}$ and UV/ZnO processes was investigated. Figure 3 indicates the change in removal efficiency of trifluralin for UV/$S_2O_8^{2-}$ and UV/ZnO processes. In the UV/$S_2O_8^{2-}$ process, the radical sulfate is produced by the anion persulfate according to the following equations [29]:

$$\begin{aligned} S_2O_8^{2-} + \mathrm{hv} &\longrightarrow 2SO_4^{\bullet-}, \\ SO_4^{\bullet-} + \text{pollutant} &\longrightarrow \text{degradation of pollutant}, \\ SO_4^{\bullet-} + H_2O &\longrightarrow HO + HSO_4^{2-}. \end{aligned} \quad (2)$$

In this research, the range of persulfate concentrations from 20 to 60 μM was investigated to determine removal efficiency of trifluralin. The results showed that by adding 20, 40, and 60 μM of persulfate to the trifluralin solution (concentration of trifluralin = 1.2 mg/L), the removal efficiency of trifluralin was 84.35 ± 15.9%, 89.091 ± 10.61%, and 92.87 ± 5.63%, respectively.

Although this trend was not significant, experiments showed that changes in the concentration of persulfate were not significantly affected to the removal efficiency. Generally, by increasing the concentration of persulfate, the amount of sulfate radicals increases as a result of ultraviolet radiation, leading to the further removal of trifluralin. However, increasing the concentration of the oxidizing agent to a certain extent can increase the reaction speed, and by increasing the concentration of oxidizing material to over optimum, the radical sulfate acts as a corrosive agent and is converted into a process for converting radical sulfate to persulfate. On the other hand, radical sulfate reacts with persulfate and produces anion sulfate, which in both cases causes the loss of radical sulfate and reduces the efficiency of removal [30].

$$SO_4^{\bullet-} + SO_4^{\bullet-} \longrightarrow S_2O_8^{2-}, \quad (3)$$

$$SO_4^{\bullet-} + S_2O_8^{2-} \longrightarrow SO_4^{-2} + S_2O_8^{\bullet-}. \quad (4)$$

In a study by Hori et al., the increase in persulfate concentrations up to a certain level reduced the release of organic pollutants due to the reaction of $SO_4^{\bullet-}$ produced by persulfate ions and the formation of SO_4^{2-} [31]. In a study by Lee et al., the effect of persulfate doses on the oxidation of diphenylamine was investigated; with the increase in the dose of persulfate up to 9 mg/L, the oxidation efficiency increased, but by increasing the dosage of persulfate to 12 mg/L sulfate did not show an increase in the oxidation process efficiency [32]. The result of Almasi et al.'s study showed that, with increasing concentrations of persulfate from 0.001 to 0.003 mol/L, the removal efficiency has increased from 53.86 to 91.17%. However, increasing concentrations of persulfate more than 0.004 mol/L did not have much effect on the removal of phenol, and the amount of organic matter removal decreased to 86.31% [33] which is similar to the results obtained in this study.

In the UV/ZnO process, the range of ZnO concentrations (50, 100, and 150 mg/L) was investigated to determine the removal efficiency of trifluralin. Increase of ZnO dose up to 50 mg/L improved the removal efficiency, but 150 mg/l of nanoparticles reduced the degradation efficiency (Figure 3(b)); also, results of the comparison of the different ZnO concentrations (initial trifluralin concentration = 0.6 mg/L) values of the removal efficiency in Figure 3(b) show that increasing the dose of the catalyst lead to higher destruction rates and higher overall decomposition of trifluralin. Thus, the efficiency of removal was 68.90 ± 10.35%, when 50 mg/l of ZnO was used, where 92.1 ± 15.58% was achieved by increasing the dose catalysts to 100 mg/l and 89.60 ± 5.63% when 150 mg/l of catalyst was used. One study reported similar results, illustrating that the excess dosage of catalyst could cause a light-screening effect that decreases the surface area of the catalyst being exposed to light irradiation and eventually decreases the photocatalytic efficiency [34]. Hoffman et al. reported that the reason for decrease in the efficiency with increasing ZnO nanoparticle concentration was the phenomenon of nanoparticle dispersion and the lack of ZnO chain production on the catalyst surface [35]. Muruganandham et al. applied ZnO nanoparticles for removing food color and found that ZnO concentration did not affect the process efficiency [36].

3.2. Effect of Trifluoralin Concentration. The effect of change in trifluralin initial concentration on trifluralin removal effciency is illustrated in Figures 4 and 5(a). As seen, the

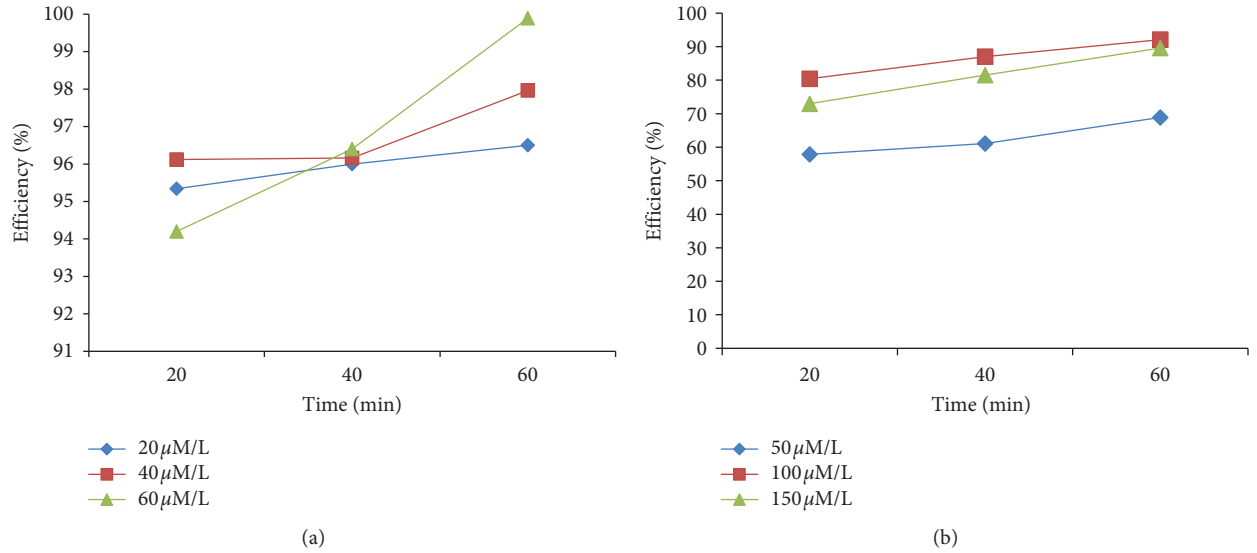

FIGURE 3: Trifluralin removal efficiency: (a) different persulfate concentrations (initial trifluralin concentration = 1.2 mg/L, pH = 9, UV = 6 W) and (b) different ZnO concentrations (initial trifluralin concentration = 0.6 mg/L, pH = 9, UV = 6 W).

mean removal percentage increased from 71.68% to 95.92%. As the trifluralin concentration increased, the removal efficiency increased because the higher concentrations of trifluralin cause the collision with radicals to increase. In this study, the initial concentrations of trifluralin in five concentrations (0.4, 0.6, 0.8, 1, and 1.2 mg/L) were studied. As shown in Figures 4 and 5(a), the highest removal efficiency in the UV/$S_2O_8^{2-}$ process was 95.92% ± 1.6 in 1.2 mg/L of trifluralin.

In UV/ZnO processes (Figures 6 and 5(b)), the highest trifluralin removal concentration is obtained in 0.6 mg/L (87.39 ± 19.22%). Increasing trifluralin concentration in the UV/ZnO process not had a constant trend in removal efficiency. In fact, ZnO has higher ability to oxidize at 0.6 mg/L trifluralin concentration compared to higher concentrations of this pesticide. UV photon absorption by ZnO nanoparticles is higher at this concentration [37]. This leads to increase in electron excitation from the valence band to conduction band [35] which will result in higher hydroxylation radical production that increases more toxicant removal. These efficiency variations are because of the formation and conversion of intermediate compounds which result in changes in UV absorption and dispersion. The increase in pesticide concentration decreases solution transparency, and consequently, the path length of the photon entering into the pesticide solution also decreases. At higher pesticide concentration, a significant amount of UV light may be absorbed by the pesticide molecule rather than the catalyst, and this may also reduce the catalytic efficiency. The rate of photodegradation is related to the formation of OH radicals which are formed through the reaction of valence band holes with adsorbed H_2O and OH^-. At high concentration of pesticides, adsorbed OH^- ions would have been replaced by pesticides which would have reduced the production of OH radicals. This maybe the reason for the reduction in reaction rate with increase in concentration of

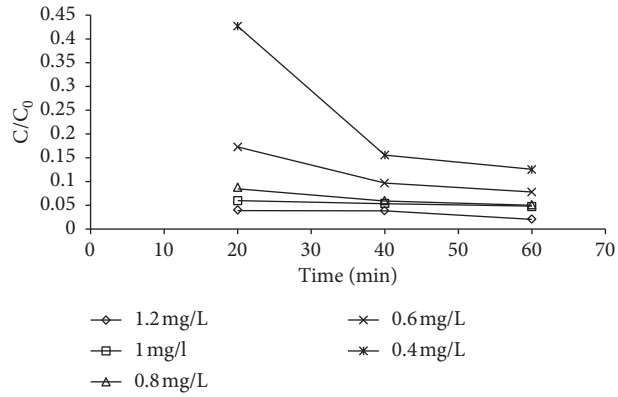

FIGURE 4: Impact of initial trifluralin concentration on process efficiency (persulfste concentration, 40 μM, PH = 9, UV = 6 W).

pesticides. In Pulmakulama et al.'s study, the highest removal efficiency in the UV/H_2O_2 method was obtained to be 6 μM between three trifluralin concentrations of 1.5, 3, and 6 μM [26]. Amit-Kumar Sharma et al. reported similar findings too [38]. Dehghani et al. studied organophosphate toxicant removal using the UV/ZnO process and reported that removal efficiency was reduced by increase of concentration [39]. Shafiei et al. worked on photocatalytic degradation of terephthalic using the UV/ZnO process and found that removal efficiency was reduced with increase of concentration due to completion of the catalyst surface [37]. As stated in these studies, due to decrease in UV penetration to the catalyst surface, removal efficiency reduced.

3.3. Effect of Contact Time. One of the effective factors in advanced oxidation processes is reaction time [40]. Time is important because reducing contact time can lead to an increase in chemical consumption. On the other hand,

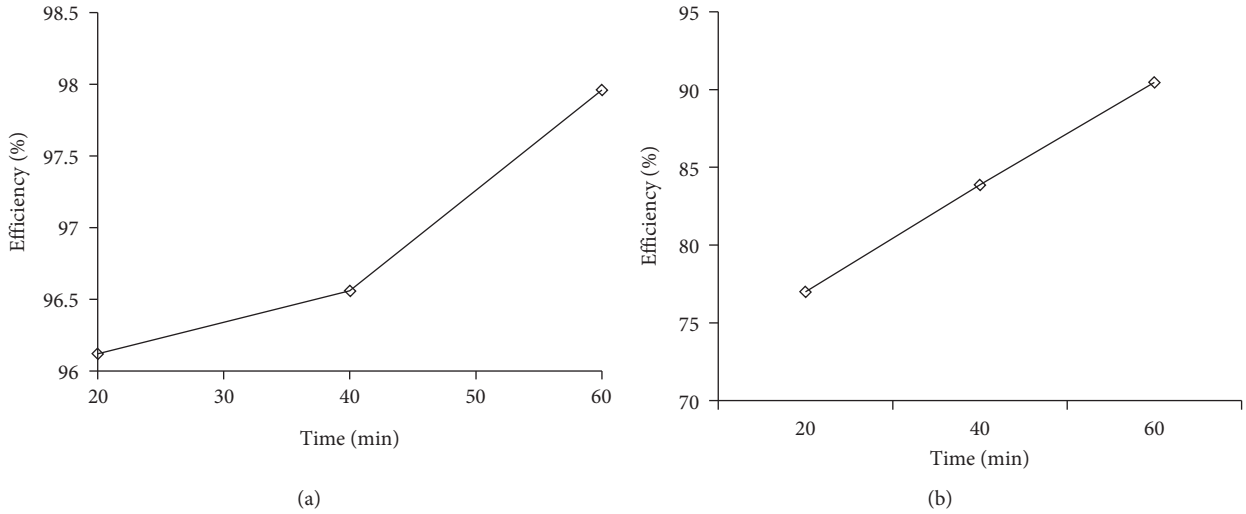

Figure 5: Trifloralin removal efficiency: (a) for 40 μM concentration of persulfate (initial trifluralin concentration: 1.2 mg/L, PH = 9, UV = 6 W) and (b) for 100 mg/L concentration of ZnO (initial trifluralin concentration: 0.6 mg/L, pH = 9, UV = 6 W).

increasing the oxidation time will increase the reactor volume and cost of construction and operation that will not be economically feasible [41]. In this study, the effect of different contact times (20, 40, and 60 min) in UV/$S_2O_8^{2-}$ and UV/ZnO processes was investigated. Trifuralin removal rate as a function of contact time is shown in Figure 5. According to this figure, in both processes, with an increase in time, the rate of photocatalytic degradation of trifuralin increases and higher effciency is obtained in higher contact times. This is due to increased interaction between hydroxyl radicals and trifuralin. Anissa Dhaouadi et al., Sergio et al., and shahsavan et al. reported similar findings. They have associated this with higher production of hydroxyl radicals by increasing the reaction time [42].

Moradi et al. worked on permethrin pesticide removal from water using chitosan/ZnO and found that increase in contact time increased the percentage of pesticides removal. This occurred due to the availability of many empty surfaces for absorption at the initial stage, and subsequently, adsorption rates reached a constant value [43] because the absorbent surface was filled after the contact time of 90 min. Daneshvar et al. studied combination of advanced oxidation and biological purification processes for pesticide removal from aqueous solutions. They reported that, with increasing contact time in the UV/ZnO process, diazinon removal increased. However, after 1.5-hour contact time, removal percentage was slightly increased [44].

3.4. Kinetic Study of UV/$S_2O_8^{2-}$ and UV/ZnO Processes. In this study, according to the optimal conditions, zero-, first-, and second-order kinetic equations (equations (5)–(7)) were used for data analysis in UV/$S_2O_8^{2-}$ and UV/ZnO processes, which are shown in Figures 7 and 8 and Table 1 summarizes the results of kinetic studies at optimal concentration of UV/$S_2O_8^{2-}$ and UV/ZnO processes. The findings exhibited that both UV/$S_2O_8^{2-}$ and UV/ZnO processes followed the zero-order kinetics.

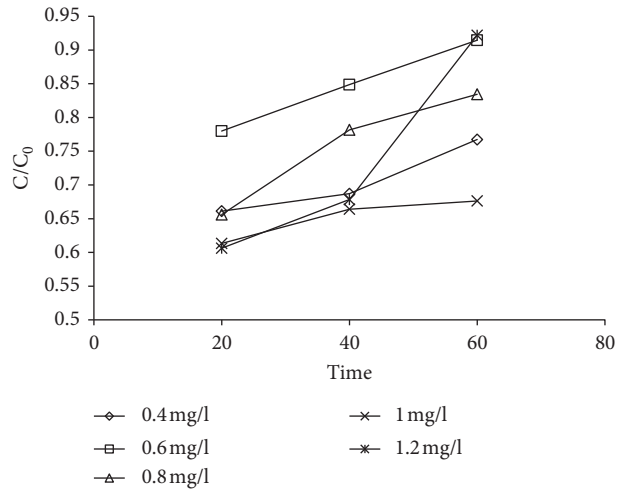

Figure 6: Effect of initial trifluralin concentration on process efficiency (ZnO concentration, 100 mg/L, pH = 9, UV = 6 W).

$$C_t = kt + C_0 \text{ zero} - \text{order equation}, \quad (5)$$

$$Ln(C_t) = -kt + Ln(C_0) \text{ first} - \text{order equation}, \quad (6)$$

$$\frac{1}{C_t} = \frac{1}{C_0} + kt \text{ second} - \text{order equation}. \quad (7)$$

In Azizi et al.'s study on the photocatalytic removal of pentachlorophenol from aqueous solutions with ZnO in the presence of UV radiation, a pseudo-first-order kinetic model was used and R^2 was found to be about 0.97 [45]. Another study reported on the O_3/UV/H_2O_2 process degradation of trifluralin followed the pseudo-first-order kinetics [46].

3.5. Chemicals. The results of the SEM image showed that the Zn nanoparticle size in this study was less than 100 nm, and the SEM technique showed no impurity in the zinc oxide nanoparticle used in this study (Figure 2).

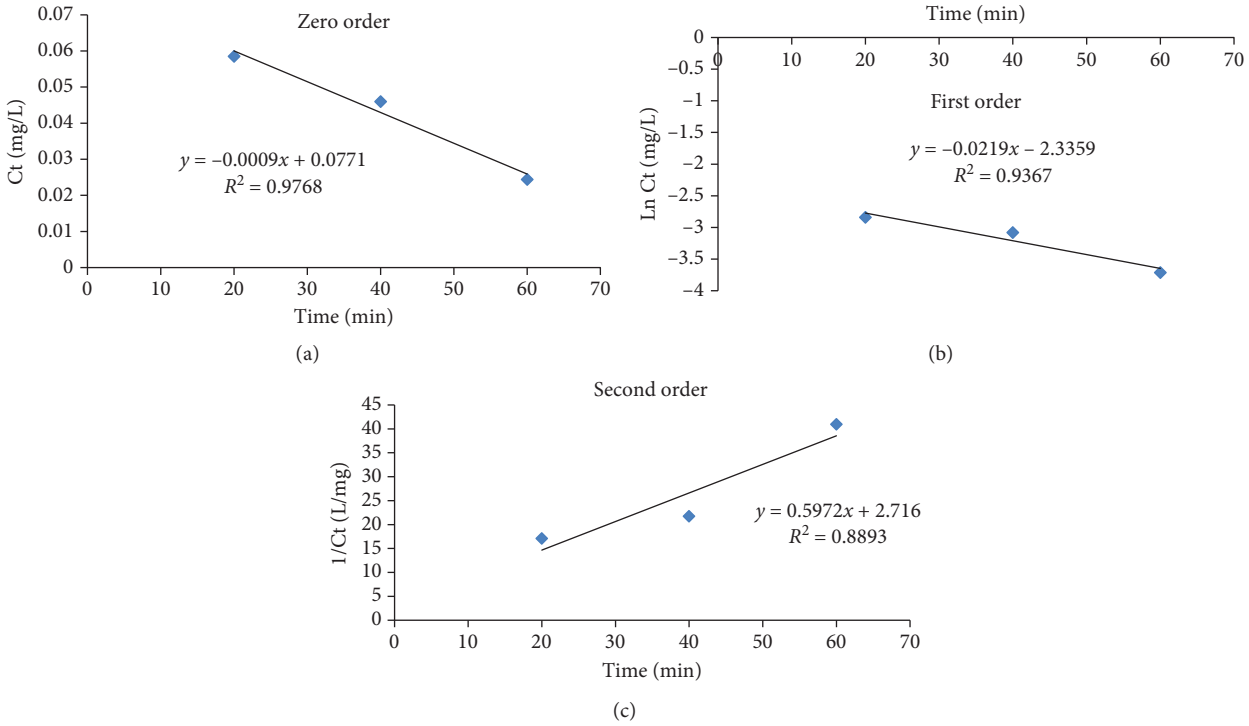

Figure 7: The rate of trifluralin removal reaction in the UV/S2O28 process (the initial concentration of trifluralin and S2O28 is 1.2 mg/L and 40 μM, respectively, pH = 9, UV = 6 W).

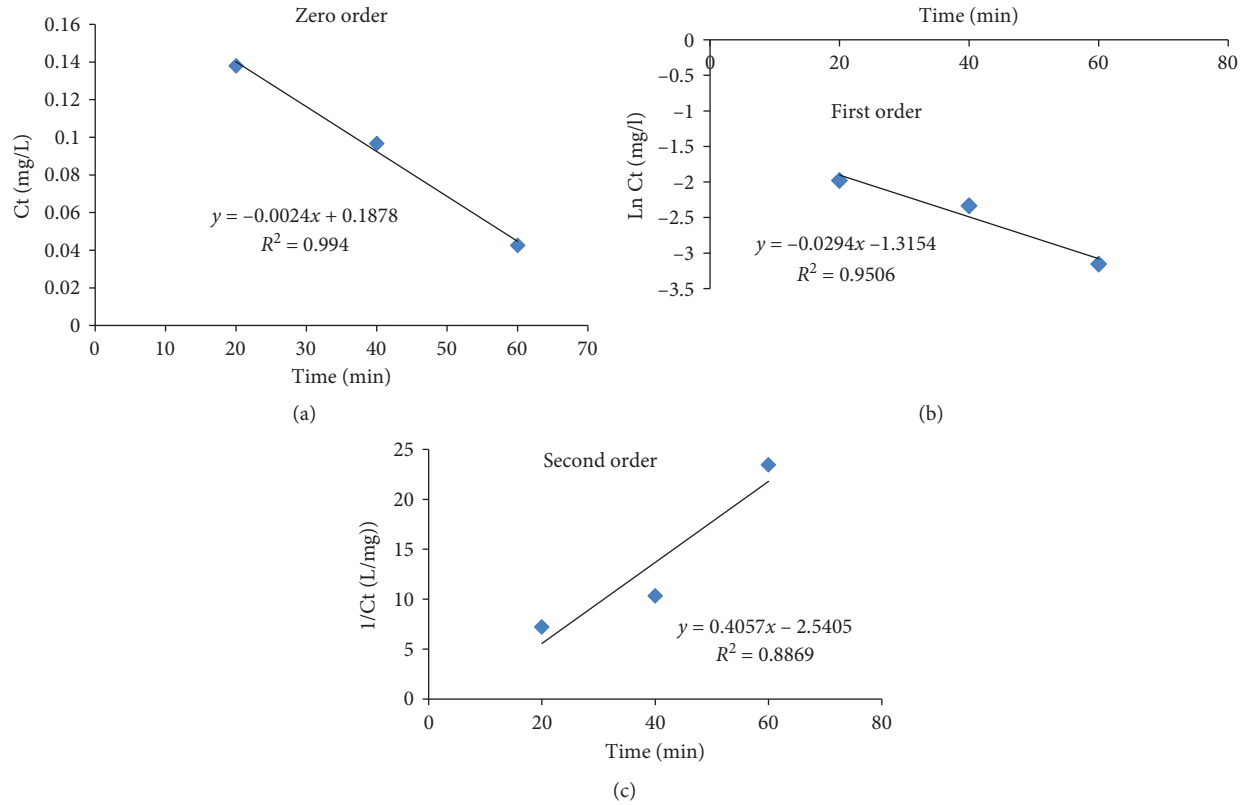

Figure 8: The rate of trifluralin removal reaction in the UV/ZnO process within optimal condition (the initial concentration of trifluralinand ZnO is 0.6 mg/L and 100 mg/L, respectively, pH = 9, UV = 6 W).

Table 1: Summary of the kinetic analysis results of trifluralin removal in optimal condition.

Kinetics	K		Unit	R^2	
	$UV/S_2O_8^{2-}$	UV/ZnO		$UV/S_2O_8^{2-}$	UV/ZnO
Zero order	−0.0009	−0.0024	mg/L.min	**0.9768**	**0.9940**
First order	−0.0219	−0.0294	1/min	0.9367	0.9506
Second order	0.5972	0.4057	L/mg.min	0.8893	0.8869

3.6. Cost Estimation of the $UV/S_2O_8^2$ and UV/ZnO Processes. AOP process is an electric-energy-intensive process, and electric energy has a major fraction of the operating costs. Study of electric energy consumption in AOP processes can be very useful. The Photochemistry Commission of the International Union of Pure and Applied Chemistry (IUPAC) has proposed an efficiency index for different AOP processes with based on UV. Electrical energy per order (EE/O) compares the electrical efficiency of different UV-based AOPs and is a measure of the electrical efficiency of an AOP system. Electric energy per order (EE/O) is defined as the electric energy in kilowatt hours (kWh) required to degrade a contaminant by one order of magnitude in a unit volume (1 m^3 or 1000 L) of contaminated water. It should be noted that EE/O was only for first-order and second-order reactions and EE/M was applied for zero-order reactions. If the degree of reaction changes, the energy equation changes [47]. In fact, the lower the EE/M, the higher the energy efficiency of the AOP process. In this study, for comparative between $UV/S_2O_8^2$ and UV/ZnO processes, the EE/M value was calculated.

$$\text{EE/M (kWh/Kg)} = \frac{P_{elec} \times t \times 1000}{V \times M \times 60 \times \left(C_{A_0} - C_A\right)}, \tag{8}$$

$$\text{EE/M (kWh/Kg)} = \frac{0.006 \times 60 \times 1000}{0.25 \times 60 \times (1.2 - 0.02448)} = 20.41\ \text{kWh/Kg}, \tag{9}$$

$$\text{EE/M (kWh/Kg)} = \frac{0.006 \times 60 \times 1000}{0.25 \times 60 \times (0.6 - 0.054)} = 43.95\ \text{kWh/Kg}, \tag{10}$$

where EE/O is the electric energy per order (kWh/m^3), EE/M is the electrical energy per unit mass (kWh/Kg), P_{elec} is the power consumption (kW), V is the volume of water in liters in the reactor, t is the irradiation time (min), C_{A0} is the initial concentration of trifluralin (mol/L), and C_A is the final concentration of trifluralin at the end of the purification time (mol/L). According to the calculations, EE/M of $UV/S_2O_8^2$ and UV/ZnO were about 43.95 and 20.41 kWh/kg, respectively. The result of daneshvar et al.'s study showed that the photocatalysis process in the presence of ZnO offered the best energy efficiency (1075.3 kWh/m^3) for diazinon removal [46].

3.7. Real-Scale Measurements. If this system is implemented at the beginning of the drinking water well and the water of the respective well is 30 L/s and a 24 W lamp is used for purification, then calculations are made as equation (8) for both $UV/S_2O^2{}_8^-$ and UV/ZnO processes.

$$\text{EE/M (kWh/Kg)} = \frac{0.024 \times 60 \times 1000}{30 \times 3600 \times 60 \times (1.2 - 0.02448) \times 0.001} = 0.189\ \text{kWh/Kg}. \tag{11}$$

As it was observed, the energy consumed per Kg of contaminated water was estimated to be 0.189 kW/h, which is economically optimal.

$$\text{EE/M (kWh/Kg)} = \frac{0.024 \times 60 \times 1000}{30 \times 3600 \times 60 \times (0.6 - 0.054) \times 0.001} = 3.703\ \text{kWh/Kg}. \tag{12}$$

As it was observed, the energy consumed per Kg of contaminated water was estimated to be 3.703 kW/h, which is economically optimal.

4. Conclusions

In this study, the comparison between UV/$S_2O_8^{2-}$ and UV/ZnO processes on trifluralin removal in optimal conditions (contact time of 60 min, the persulfate concentration of 40 μm, and ZnO concentration of 100 mg/L) was made. The optimal trifluraline concentrations were 1.2 mg/L and 0.6 mg/L for UV/$S_2O_8^{2-}$ and UV/ZnO processes, respectively. This study proved the trifluralin removal of $92.90 \pm 1.6\%$ and $87.91 \pm 19.22\%$ for UV/$S_2O_8^{2-}$ and UV/ZnO processes in the best operation conditions. In both processes, the removal efficiency of trifluralin increased significantly with increase in contact time. However, in this process, changes in the persulfate concentration did not have much effect on the removal efficiency. In the UV/ZnO process, increasing trifluraline and ZnO concentrations did not affect trifluralin removal efficiency. The findings exhibited that both processes UV/$S_2O_8^{2-}$ and UV/ZnO followed the zero-order kinetics. The electrical energy consumed of UV/$S_2O_8^{2}$ and UV/ZnO was about 43.95 and 20.41 kWh/kg, respectively. In general, it can be said that, with considering the purification targets and standards for wastewater disposal, this process can be used as the final treatment of wastewater or pretreatment on a wider scale.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

This work was supported by the research deputy of Shahrekord University of Medical Sciences (Grant no. 3339). The authors, hereby, acknowledge all the university experts who provided assistance to make this study possible.

References

[1] A. Parsaie and A. H. Haghiabi, "Computational modeling of pollution transmission in rivers," *Applied Water Science*, vol. 7, no. 3, pp. 1213–1222, 2017.

[2] P. Du, X. Wu, J. Xu, F. Dong, X. Liu, and Y. Zheng, "Effects of trifluralin on the soil microbial community and functional groups involved in nitrogen cyclingfluralin on the Soil Microbial Community and Functional Groups Involved in Nitrogen Cycling," *Journal of Hazardous Materials*, vol. 353, pp. 204–213, 2018.

[3] K. C. Harrington and H. Ghanizadeh, "Herbicide application using wiper applicators - a review," *Crop Protection*, vol. 102, pp. 56–62, 2017.

[4] M. Haghighi, M. Irandoust, and M. Shariati-rad, "Simultaneous determination of antinonin and trifluralin by electrochemical method and net analyte signal interferent modeling," *Microchemical Journal*, vol. 146, pp. 34–40, 2019.

[5] L. Cao, Y. Liu, C. Xu et al., "Biodegradable poly (3-hydroxybutyrate-co-4-hydroxybutyrate) microcapsules for controlled release of trifluralin with improved photostability and herbicidal activity," *Materials Science and Engineering: C*, vol. 102, pp. 134–141, 2019.

[6] V. Triantafyllidis, S. Manos, D. Hela, M. George, and I. Konstantinou, "Persistence of trifluralin in soil of oilseed rape fields in western Greece," *International Journal of Environmental and Analytical Chemistry*, vol. 90, no. 3-6, pp. 344–356, 2010.

[7] H. Yuan, G. Ruan, Z. Chen, W. Zhang, X. Jiang, and F. Du, "A porous carbon absorbent based on high internal phase emulsion for separation and enrichment of trifluralin from soil," *Microchimica Acta*, vol. 187, no. 2, pp. 1–8, 2020.

[8] J. S. Van Dyk, B. Pletschke, and B. Pletschke, "Review on the use of enzymes for the detection of organochlorine, organophosphate and carbamate pesticides in the environment," *Chemosphere*, vol. 82, no. 3, pp. 291–307, 2011.

[9] A. Grube, D. Donaldson, T. Kiely, and L. Wu, *Pesticides Industry Sales and Usage*, pp. 1–41, US EPA, Washington, DC, USA, 2011.

[10] A. R. Ribeiro, O. C. Nunes, M. F. R. Pereira, and A. M. T. Silva, "An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched directive 2013/39/Eu," *Environment International*, vol. 75, pp. 33–51, 2015.

[11] J. E. Barbash and E. A. Resek, *Pesticides in Ground Water: Distribution, Trends, and Governing Factors*, Ann Arbor Press, Michigan, MI, USA, 1996.

[12] P. Chelme-Ayala, M. G. El-Din, and D. W. Smith, "Degradation of bromoxynil and trifluralin in natural water by direct photolysis and uv plus H2o2 advanced oxidation process," *Water Research*, vol. 44, no. 7, pp. 2221–2228, 2010.

[13] A. Le Person, A. Mellouki, A. Muñoz, E. Borras, M. Martin-Reviejo, and K. Wirtz, "Trifluralin: photolysis under sunlight conditions and reaction with Ho radicals," *Chemosphere*, vol. 67, no. 2, pp. 376–383, 2007.

[14] P. Chelme-Ayala, M. G. El-Din, and D. W. Smith, "Kinetics and mechanism of the degradation of two pesticides in aqueous solutions by ozonation," *Chemosphere*, vol. 78, no. 5, pp. 557–562, 2010.

[15] M. Arbabi, B. Mayahi, and S. Hemati, "Optimization of uv/H2o2/Fe3o4 process to remove aniline from aqueous solutions using central composite methodology," *Desalination and Water Treatment*, vol. 136, pp. 252–258, 2018.

[16] S. Martinez, M. Delgado, and P. Jarvis, "Removal of herbicide mecoprop from surface water using advanced oxidation processes (aops)," *International Journal of Environmental Research*, vol. 10, no. 2, pp. 291–296, 2016.

[17] F. Mohammadi-Moghadam, M. Sadeghi, and N. Masoudipour, "Degradation of cyanide using stabilized S, N-Tio2 nanoparticles by visible and sun light," *Journal of Advanced Oxidation Technologies*, vol. 21, no. 1, pp. 1–12, 2018.

[18] X. He, A. A. de la Cruz, K. E. O'Shea, and D. D. Dionysiou, "Kinetics and mechanisms of cylindrospermopsin destruction by sulfate radical-based advanced oxidation processes," *Water Research*, vol. 63, pp. 168–178, 2014.

[19] M. Trojanowicz, A. Bojanowska-Czajka, I. Bartosiewicz, and K. Kulisa, "Advanced Oxidation/Reduction Processes treatment for aqueous perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS) - a review of recent advances," *Chemical Engineering Journal*, vol. 336, pp. 170–199, 2018.

[20] S.-J. Kim, S.-C. Kim, S.-G. Seo, D.-J. Lee, H. Lee, and S.-C. Jung, "Photocatalyzed destruction of organic dyes using microwave/uv/O3/H2o2/tio2 oxidation system," *Catalysis Today*, vol. 164, no. 1, pp. 384–390, 2011.

[21] P. Veerakumar, K. Salamalai, N. Dhenadhayalan, and K. C. Lin, "Catalytic activity of bimetallic (Ruthenium/Palladium) nano-alloy decorated porous carbons toward reduction of toxic compounds," *Chemistry - An Asian Journal*, vol. 14, no. 15, pp. 2662–2675, 2019.

[22] M. Klavarioti, D. Mantzavinos, and D. Kassinos, "Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes," *Environment International*, vol. 35, no. 2, pp. 402–417, 2009.

[23] P. Veerakumar, A. Sangili, K. Saranya, A. Pandikumar, and K.-C. Lin, "Palladium and silver nanoparticles embedded on zinc oxide nanostars for photocatalytic degradation of pesticides and herbicides," *Chemical Engineering Journal*, vol. 410, Article ID 128434, 2021.

[24] E. S. Elmolla and M. Chaudhuri, "Degradation of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution by the uv/zno photocatalytic process," *Journal of Hazardous Materials*, vol. 173, no. 1-3, pp. 445–449, 2010.

[25] M. H. Dehghani, M. Mahmoodi, and A. Zarei, "Toxicity study of uv/zno treated solution containing reactive blue 29 using Daphnia magna as a biological indicator," *MethodsX*, vol. 6, pp. 660–665, 2019.

[26] J. Behin and N. Farhadian, "Response surface methodology for ozonation of trifluralin using advanced oxidation processes in an airlift photoreactor," *Applied Water Science*, vol. 7, no. 6, pp. 3103–3112, 2017.

[27] P. Chelme-Ayala, M. G. El-Din, D. W. Smith, and C. D. Adams, "Oxidation kinetics of two pesticides in natural waters by ozonation and ozone combined with hydrogen peroxide," *Water Research*, vol. 45, no. 8, pp. 2517–2526, 2011.

[28] Y. Shiying, P. Wang, X. Yang, W. Guang, W. Y. Zhang, and S. Liang, "A novel advanced oxidation process to degrade organic pollutants in wastewater: microwave-activated persulfate oxidation," *Journal of Environmental Sciences*, vol. 21, no. 9, pp. 1175–1180, 2009.

[29] A. Sidmohammadi, G. H. Asgari, A. Ebrahimi, Z. Sharifi, and H. Movahedian, "4-Chlorophenol oxidation combined with the application of advanced oxidation technology and the modified microwave in chemical and petrochemical wastewater industry," *Health System Research*, vol. 3, pp. 390–396, 2010.

[30] A. Esrafili, R. R. Kalantary, A. Ali, E. Ahmadi, and M. Gholami, "Removal of diethyl phthalate from aqueous solution using persulfate-based (uv/Na2s2o8/Fe2+) advanced oxidation process," *Journal of Mazandaran University of Medical Sciences*, vol. 25, no. 132, pp. 122–135, 2016.

[31] H. Hori, A. Yamamoto, E. Hayakawa et al., "Efficient decomposition of environmentally persistent perfluorocarboxylic acids by use of persulfate as a photochemical oxidant," *Environmental Science & Technology*, vol. 39, no. 7, pp. 2383–2388, 2005.

[32] C. S. Liu, K. Shih, C. X. Sun, and F. Wang, "Oxidative degradation of propachlor by ferrous and copper ion activated persulfate," *Science of the Total Environment*, vol. 416, pp. 507–512, 2012.

[33] H. Almasy, A. G. Asghari, M. Leili, Z. Sharifi, and S. M. Abdolmotalb, "Study on the removal of phenol from aqueous solutions by exogenous oxidizing agents of peroxide, peroxide, and peridate activated by ultrasound," *Journal of Rafsanjan University of Medical Sciences*, vol. 15, no. 9, pp. 835–848, 2016.

[34] M. Shokri, G. Isapour, M. A. Behnajady, and S. Dorosti, "A comparative study of photocatalytic degradation of the antibiotic cefazolin by suspended and immobilized TiO2nanoparticles," *Desalination and Water Treatment*, vol. 57, no. 27, pp. 12874–12881, 2016.

[35] M. R. Hoffmann and S. T. Martin, "Wonyong choi, and detlef W bahnemann. "Environmental applications of semiconductor photocatalysis," *Chemical Reviews*, vol. 95, no. 1, pp. 69–96, 1995.

[36] N. Assi, P. A. Azar, M. Saber Tehrani, S. W. Husain, D. Maher, and S. Pourmand, "Synthesis of zno-nanoparticles by microwave assisted sol-gel method and its role in photocatalytic degradation of food dye tartrazine (acid yellow 23)," *International Journal of Nano Dimension*, vol. 8, no. 3, pp. 241–249, 2017.

[37] A. Shafaei, M. Nikazar, and M. Arami, "Photocatalytic degradation of terephthalic acid using titania and zinc oxide photocatalysts: comparative study," *Desalination*, vol. 252, no. 1-3, pp. 8–16, 2010.

[38] A. K. Sharma, R. K. Tiwari, and M. S. Gaur, "Nanophotocatalytic uv degradation system for organophosphorus pesticides in water samples and analysis by kubista model," *Arabian Journal of Chemistry*, vol. 9, pp. S1755–S1764, 2016.

[39] M. H. Dehghani and A. M. Fadaei, "Potoccatalytic oxidation of oganophosphorus pesticides using zinc oxide," *Research Journal of Chemistry and Environment*, vol. 16, pp. 104–109, 2012.

[40] S. Wang, N. Zhou, S. Wu, Q. Zhang, and Z. Yang, "Modeling the oxidation kinetics of sono-activated persulfate's process on the degradation of humic acid," *Ultrasonics Sonochemistry*, vol. 23, pp. 128–134, 2015.

[41] S. Dehghani, A. Jafari Jonidi, M. Farzadkia, and M. Gholami, "Investigation of the efficiency of fenton's advanced oxidation process in sulfadiazine antibiotic removal from aqueous solutions," *Journal of Arak University Medical Sciences*, vol. 15, no. 7, pp. 19–29, 2012.

[42] S. Pérez-Sicairos, K. A. Corrales-López, O. M. Hernández-Calderón, M. I. Salazar-Gastélum, and R. M. Félix-Navarro, "Photochemical degradation of nitrobenzene by S2o8–2 ions and uv radiation," *Revista Internacional de Contaminación Ambiental*, vol. 32, no. 2, pp. 227–236, 2016.

[43] S. M. Dehaghi, B. Rahmanifar, M. Ali, and P. A. Azar, "Removal of Permethrin pesticide from water by chitosan–zinc oxide nanoparticles composite as an adsorbent," *Journal of Saudi Chemical Society*, vol. 18, no. 4, pp. 348–355, 2014.

[44] N. Daneshvar, D. Salari, A. Niaei, and A. R. Khataee, "Photocatalytic degradation of the herbicide erioglaucine in the presence of nanosized titanium dioxide: comparison and modeling of reaction kinetics," *Journal of Environmental Science and Health, Part B*, vol. 41, no. 8, pp. 1273–1290, 2006.

[45] S. Azizi and M. Samarghandi, "Evaluation of the photocatalytic removal of Pentachlorophenol by uv/zno from aqueous solutions," *Razi Journal University Medical Scencesi*, vol. 135, no. 22, pp. 38–52, 2015.

[46] N. Daneshvar, S. Aber, M. Seyeddorraji, A. Khataee, and M. Rasoulifard, "Photocatalytic degradation of the insecticide diazinon in the presence of prepared nanocrystalline zno powders under irradiation of uv-C light," *Separation and Purification Technology*, vol. 58, no. 1, pp. 91–98, 2007.

[47] N. N. Mahamuni and Y. G. Adewuyi, "Advanced oxidation processes (aops) involving ultrasound for waste water treatment: a review with emphasis on cost estimation," *Ultrasonics Sonochemistry*, vol. 17, no. 6, pp. 990–1003, 2010.